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Abstract

A new code, named Hybrid Molecular Dynamics – Kinetic Monte Carlo (Hybrid MD/KMC), has been developed and employed to analyze possible growth pathways that lead to high molecular mass compounds. The Hybrid MD-KMC code combines the strengths of two common simulation methods: Kinetic Monte Carlo, and Molecular Dynamics. This code puts the two simulation procedures on an equal footing and involves alternating between MD and KMC steps during the simulation. The strength of this approach is that it provides information on the physical as well as chemical structure of soot precursors providing at the long term potential for information on particle characteristics such as density, porosity, and other physical properties. The Kinetic Monte Carlo and Molecular Dynamics simulation are used in conjunction with high-level quantum chemical calculations.

Introduction

This paper is directed at the development of a new tool for examining the molecular transformations from gas phase precursors to soot. Although H-abstraction-Carbon-addition pathways for soot formation is well established, there is increasing evidence for a parallel polymerization pathway [1-7]. Recently we developed a kinetic mechanism in which high

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molecular mass aromatic compounds are postulated to form by the reactive polymerization of small PAH [4,8-10]. The mechanism involves a sequence of chemical reactions between aromatic compounds with 6 π-electron, i.e. benzene, naphthalene, and compounds containing conjugated double bonds i.e., acenaphthylene, cyclopentadiene, indene. The distinguishing features of this mechanism and its importance in explaining experimental observations is reported elsewhere [9]. The acetylene addition and polymerization routes for soot formation probably occur in parallel in relative amounts that depend on the fuel and the combustion conditions. The polymerization reactions are frequently expressed in generalized global terms such as $A_i + A_j = A_{i+j}$. Recently several papers have addressed the chemical details of the elementary steps for this global polymerization reaction [9-10].

The main thrust of this article is to provide the missing microscopic detail of the molecule growth, which is experimentally inaccessible, using large-scale, statistical mechanics simulations and Molecular Dynamics, in conjunction with high level quantum chemical calculations. The strength of this approach is that it provides information on the physical as well as chemical structure of soot precursors providing at the long term potential for information on particle characteristics such as density, porosity, and other physical properties.

After summarizing in the following section the methodological details of the computations performed, we will provide results from the quantum chemical calculations and from the use of the Hybrid MD-KMC code.

Method

The Hybrid MD-KMC method here proposed combines the strengths of two common simulation methods: Kinetic Monte Carlo (KMC) [11] and Molecular Dynamics (MD) [12]. This code puts the two simulation procedures on an equal footing and involves alternating between MD and

KMC steps during the simulation [13]. This method allows sampling long time-scales, where the time-duration between Monte Carlo events can be arbitrarily long (depending on the kinetics, model. etc), while in molecular dynamics, we require time steps which are a small fraction of the atomic vibrational period. So the combination of the two techniques spans two time- and equilibrium scales, MD allows for relaxation as well as processes very far from equilibrium, while the KMC part allows much larger time-scale changes to the system, provided that the system is at equilibrium. The time-step for a single KMC iteration is a "real time," determined by the kinetics system. The result is a rapidly convergent method, which is able to solve the sampling problem with many organic molecules and complexes. The reaction rates among the compounds present in the system are specified as probabilities and the surface configuration over time is then given by a master equation, describing the time evolution of the probability distribution of system configurations.

Structure simulation

Simulation parameters

There are three basic modules that determine the evolution of the structure. They are: *(a)* the reaction site module, *(b)* the gas-phase module, and *(c)* the kinetic rate expression module. *(a)* The reaction site module governs the definition and counting algorithm of reaction sites, which are capable of undergoing modification (for example, addition reactions). Reaction sites have been defined in the context of the empirical bond-order potentials of Brenner [14], which is able to capture many of the essential features of chemical bonding in hydrocarbons. The analytical function is a highly parametrized version of Tersoff's empirical-bond-order formalism [15]. Nonlocal effects have been incorporated via an analytic function that defines conjugation based on the coordination of carbon atoms that neighbor carbon-carbon bonds. Because only

nearest-neighbor interactions are incorporated, the function is very quickly evaluated and can therefore be used in large-scale molecular-dynamics simulations. The following sites have been defined in this study: (1) H atom on a 5-membered ring, (2) H atom on a 6-membered ring, (3) dangling bond on a 5-membered ring, (4) dangling bond on a 6-membered ring, (5) sp^3 Hydrogen, (6) HCCCCR chains prone to close to form 5-membered rings, (7) HCCCCCR chains prone to close to form 6-membered rings, (8) HCCCCCH chains prone to close to form 5-membered rings, and (9) HCCCCCCH chains prone to close to form 6-membered rings. In the chains, R is a radical carbon. Examples of these sites are shown in Fig.1.

Bonding pairs are defined according to the formalism of Brenner. Hence, chains and rings are identified through efficient nested loops directed by neighbor list pointers. Additional proximity and geometric conditions are placed on the definition of the HC..CH chains to ensure that false-positive sites are not identified. Proximity conditions are also placed on radical sites. In the site-counting procedure, a radical carbon is considered as a possible site for termination or addition by a gas-phase species only if the gas-phase species of interest can be accommodated.

(b) In the gas-phase module, the user must define the number and concentrations of the gas-phase species present in the environment.

(c) The third module driving the particle evolution is the kinetic rate constant module. Reactions and kinetic rate constants are introduced as a function of time, temperature, pressure, and molecular weight. The configurations are stochastically integrated according to the kinetics we provide. A transition event is selected randomly, with its weight proportional to its kinetic rate. This rate for a typical gas-surface reaction, is

$$r = k\, C_g\, N_s \qquad (1)$$

where k is the pressure and temperature dependent rate constant, C_g is the gas-phase concentration, while N_s is the surface-site density or number for a particular reaction in which

gas-species g reacts with a particular surface site s. The real structure of a compound is decomposed into one that is defined by an array of surface positions.

Algorithmic approach

The modification to the particle is determined by the solution to the Master equation, which is given in Equation (2),

$$\frac{dP_\alpha}{dt} = \sum_\beta \left(W_{\beta\to\alpha} P_\beta - W_{\alpha\to\beta} P_\alpha \right) \qquad (2)$$

where P_α (P_β) is the probability of finding the system in configuration α (β), the W's are transition probabilities per unit time for various reactions[16]. The weighted transition probabilities are given as the normalized rates of all possible reactions/transitions calculated using the three modules discussed previously. Once the reaction and reaction site are determined, the structure is modified appropriately. For H-abstraction reactions here, hydrogen atoms are simply removed from the list of existing atoms, and the particle is then subjected to relaxation for 2 ps using the molecular dynamics module. For addition and termination reactions, atoms are added at the reaction site in reasonable configurations. This is followed by constrained relaxation for 2 ps, in which the length of the bond between the particle and the newly added species is constrained. After this, an unconstrained relaxation for 2 ps is also performed. Ring closure reactions have been introduced into the code to form five and six-rings, involve a longer procedure, in which the C-C distance between the ends of the chain are gradually brought together, while all other atoms are allowed to relax. We have found reliable results by using increments of 5E-6 Angstroms for closing the rings. After the ring has been closed, full relaxation is performed for 2 ps. At this point, the molecule is ready for the next iteration in which the reaction sites of the new updated particle are counted.

Each iteration in the Hybrid MD-KMC code goes as follows:

1. take gas-phase concentrations (typically from the user or another application),
2. perform site-counting procedure – identify every atom with a local environment which fits the definition of each site – check if there is enough room next to the site for a gas-phase specie to penetrate and react,
3. evaluate the kinetic rate constants ($k = A\ T^n \exp(-Ea/RT)$) and the reaction rates ($r = k\ C_g N_s$). The kinetics have been calculated through electronic structure calculations, see next section,
4. select reaction with probability proportional to its rate,
5. randomly select the first site for the reaction chosen,
6. perform modification of site according to the reaction transition (move a H for abstraction, add some species, etc),
7. perform energy minimization

Reaction kinetics

Kinetic parameters for the possible reactions among the species present in the systems have been evaluated using the Transition State Theory (TST) [17], and the Evan–Polanyi linear free-energy formula [18] within the reaction class TST formalism, to provide activation energies of reactions in a given reaction class. The potential energy information were calculated using the hybrid density functional B3LYP method [19] (i.e. B3LYP/6-31G(d,p) [20-21-22]).

Conditions

High molecular mass compound growth is modeled in the environment of a low-pressure (2.67 kPa) laminar premixed benzene/oxygen/argon flame of Bittner and Howard [23] for an

equivalence ratio of 1.8. The temperature and some specific PAH (naphthalene, and acenapthylene) that will be used as input to the HMC code have been calculated using the CHEMKIN package [24] together with a kinetic model previously developed [25] and are compared with the experimental data in Fig.2. The choice of these PAH is due to their presence in high concentrations in the PAH inventory, and to the importance that PAH with peripherally fused five-membered rings (CP-PAH), which include acenaphthylene, have in the flame formation chemistry of soot [26-32] and fullerenes [33]. In using these concentrations in the HMC code, no allowance was made in the calculated PAH and H profiles for species depletion or temperature change.

Bittner and Howard also measured the signal from species larger than 200u in flame [23], which shows a rapid increase starting at a distance of 4 mm above the burner, reaching a maximum at 8 mm from the burner. We are interested in following the growth of such high molecular mass compounds, and therefore we decided to start our simulation with HMC from a temperature of 1400K that corresponds to that distance at which the 200u signal appears.

Results and Discussion

Results using quantum chemical approach

The sequence for aromatic growth begins with the H-abstraction from aromatic compounds to produce the corresponding radical [9] that furnishes higher aromatics through a two-step radical-molecule propagation step that involves addition reactions. Iteration of this mechanism followed by rearrangement of the carbon framework ultimately leads to the formation of high molecular mass compounds [4,10].

The Evan–Polanyi linear free-energy formula [34] was used to derive the activation energies in a given reaction class. H-abstraction reaction rates for the reaction of acenaphthrylene,

cyclopenta[cd]pyrene, anthracene, and pyrene to form the corresponding radical and H_2 is reported elsewhere [35]. Figure 3 reports the activation barriers for a number of propagation step reactions versus the heat of reaction. The data in the graph show the relation for the addition of phenyl, and naphthyl radicals to cyclopentafused PAH (cyclopentadiene, acenaphthylene, and aceanthrylene…). The results obtained show agreement with the Hammond postulate: as the reactions become more exothermic, the energetic barriers are lower and shifted towards the reactants.

As input information for the kinetic rate expression module to the HMC code, we added also reaction rates for ring closure. It is interesting to be able to simulate also the growth of curved polycyclic aromatic hydrocarbons (PAH) composed of five- and six-membered rings, that are possible candidates for the starting material of fullerenes. To do so, the same analysis done for the propagation step using the Evans-Polanyi model, has been repeated for the ring closure chemistry that leads to the increased extension of aromatic islands inside the structure. As an example of these calculations, we report the energy profile for ring closure and dehydrogenation involving H1 and H2 for *Structure a* reported in Fig. 4, obtained by the addition of 1-naphthyl to the double bond of acenaphthylene.

Through a first transition state *(TS1)* a bond is formed between C3 and C4 that brings to the formation of a six-membered ring (*Structure b*). The ring closure is endothermic by ca. 2.86E-1 kcal/gr. The connection between *(TS1) – Structure b – (TS2)* is confirmed by intrinsic reaction coordinate (IRC) calculations. From *Structure b* the reaction continues by elimination of H_2. The atoms H1 and H2 are now both in the same plane and their distance of separation is 1.9 A. In the final configuration *Structure c* the two H atoms have been eliminated. For this process the reaction rate is $k = 5.48E+10\ T^{1.07} \exp(-4.87E+4/T)\ [s^{-1}]$

Results using Hybrid Monte Carlo method

The results obtained through DFT calculations in terms of reaction rates have been plugged into the HMC code. Starting from a gas-phase bulk containing acenaphthylene, naphthalene and H, the calculations follow the growth of an individual substrate (in this case naphthalene) to which compounds from the bulk are added. A transition event is selected randomly, with its weight proportional to its kinetic rate. HMC allows sampling long time-scales, where the time-duration between Monte Carlo events can be arbitrarily long (depending on the kinetics, model. etc), while in molecular dynamics, we require time steps which are a small fraction of the atomic vibrational period. MD allows for relaxation, while the KMC part allows much larger time-scale changes to the system.

In order to better describe the methodology, and to highlight the importance of Molecular Dynamics in this method, we analyze the structure reported in Fig.5. The compound $C_{44}H_{24}$ represents an intermediate produced during the molecular growth process, and it was obtained from $C_{44}H_{25}$ through H-abstraction from C1. In this case the hydrogen atom is simply removed from the list of existing atoms, and the particle is then subjected to relaxation for few psec using the molecular dynamics module, that allows the structure to reach a relaxed local minimum. Figure 5 shows the changes that occur to the structure during the first 2 ps of relaxation (dashed line – after 1 ps; solid line – after 2 ps).

The calculations on molecular configurations can provide information on the proximity of H atoms and the probable sites for ring closure.

After the application of the Molecular Dynamics, new potential reactions and reaction sites are identified, and the Kinetic Monte Carlo module is applied for a given interval to calculate the new structures formed. All possible combinations are considered with appropriate weighting to the probability of reaction based on kinetic rate constant and reactant concentrations. Examples

of structural evolutions of high molecular mass compounds are shown in Fig. 6 for the system selected (starting compound is naphthalene).

Structure 2 ($C_{64}H_{38}$) is formed from Structure 1 through H abstraction and further addition of 2 molecules of naphthalene and 1 acenaphthalene. The addition sites for the compounds are highlighted to help the reader. After further H abstraction and naphthalene addition, Structure 3 ($C_{104}H_{57}$) is produced. Structure 4 has a formula of $C_{126}H_{69}$ and a ring closure reaction has occurred (the site is evidenced).

The introduction of ring closure reactions by dehydrogenation in the kinetic scheme allows the formation of curved structures. The H/C ratio of the structures slowly decreases going from 0.57 for the first structure to 0.53 for the last in the present limited simulation. Ultimately further dehydrogenation reactions lead to the carbon nanoparticles such as soot and fullerenes.

Evidences for molecules such as shown in Fig.6 is provided by Homann and co-workers [36], who analyzed large PAH molecules and radicals in a low-pressure benzene-oxygen flame (C/O=0.8, v=42 cm s-1 P=2.66KPA), using molecular beam time-of-flight mass spectrometry combined with resonance enhanced multi-photon ionization (REMPI). They reported a C-H diagram for each molecular formula C_xH_y identified in flame for PAH and PAH radicals. The combination of the polymerization mechanism together with HMC code allow us to build compounds with H/C ratios in the range identified by the authors, and to provide information on the chemical structure. For example, the compounds $C_{32}H_{18}$, and $C_{44}H_{24}$, etc produced by the code have H/C ratios of soot precursors in the range identified by Homann and coworkers [36], and that are much higher than those of polybenzenoid structures of equal molecular weight.

A larger number of simulations can give statistically information about the system, i.e. H/C and molecular weight distribution, moieties, cross-linking characteristics as function of the time.

Discussion and Conclusions

This paper is directed at the development of a new tool for examining the molecular transformations from gas phase precursors to soot. A new code, named Hybrid Monte Carlo (HMC), has been developed and employed to analyze possible growth pathways that lead to high molecular mass compounds. The Hybrid Monte Carlo (HMC) method here proposed combines the strengths of 2 common simulation methods: Kinetic Monte Carlo (KMC), and Molecular Dynamics. This code puts the two simulation procedures on an equal footing and involves alternating between MD and MC steps during the simulation. This method allows sampling long time-scales, where the time-duration between Monte Carlo events can be arbitrarily long (depending on the kinetics, model. etc), while in molecular dynamics, we require time steps which are a small fraction of the atomic vibrational period. The features of the two methods have been illustrated with detailed examples in the previous section.

To shed light on the mechanism of hydrocarbon growth, Kinetic Monte Carlo – Molecular Dynamic simulations, in conjuction with high level quantum chemical calculations were carried out with concentration of the relevant precursor molecules, temperature, and time representative of combustion conditions. The environment chosen for this analysis is a low-pressure laminar premixed benzene/oxygen/argon flame studied by Bittner and Howard. The open structures obtained with the reaction scheme presented above and the HMC code provide an explanation for the H/C ratios of soot precursors and young soots being greatly higher than those of polybenzenoid structures of equal molecular weight. Also, the curvature introduced by forming five- and six-membered rings is the most noticeable feature of these structures.

The knowledge of the structures of soot precursor compounds is important to further progress with respect to the question about soot formation models by applying the HMC code to follow the time-evolution of a statistical ensemble of molecules, as well as the time-evolution of

extremely large molecules. Chemical characteristics like H/C [36], moieties measurable by NMR [37] and LMMA [38] can be evaluated through a large number of simulations using HMC code. In addition physical properties such as density, and porosity [39] can be calculated from the chemical structure.

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Figure Captions:

Fig. 1: Reaction sites defined in the HMC code.

Fig. 2: Comparison between the modeled concentration profiles of naphthalene, acenaphthylene and H and experimental data for C_6H_6 low pressure flame [32].

Fig. 3 Activation barriers versus the heat of reaction for a number of propagation step reactions. The data show the relation for the addition of phenyl, and naphthyl radicals to the class of cyclopentafused hydrocarbons.

Fig. 4: Relative energy ΔE (kcal/mol) diagram for ring closure and dehydrogenation involving H1 and H2 from Structure *a* together with the optimized structures.

Fig. 5: Intermediate $C_{44}H_{24}$ formed during the HMC simulation.

Fig 6: Structural evolutions of high molecular mass compounds using HMC code.

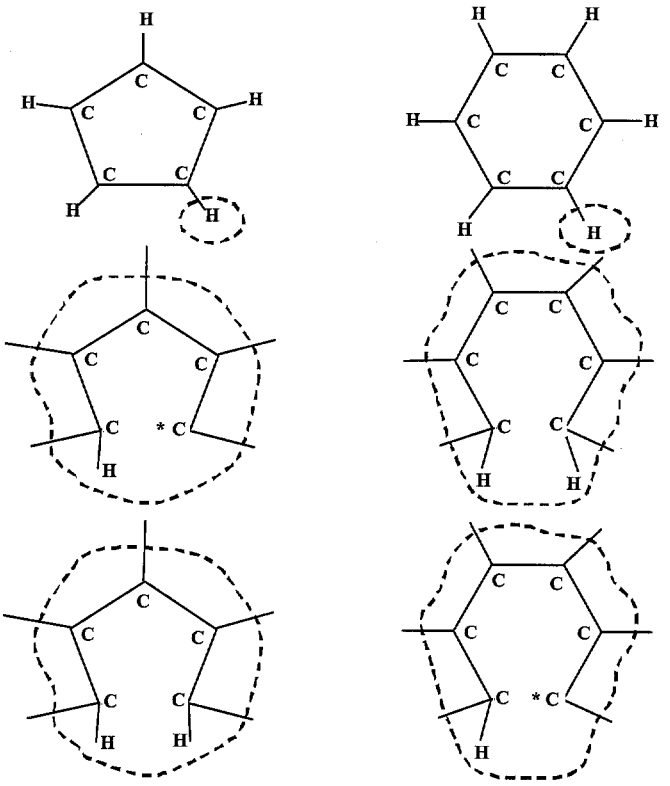
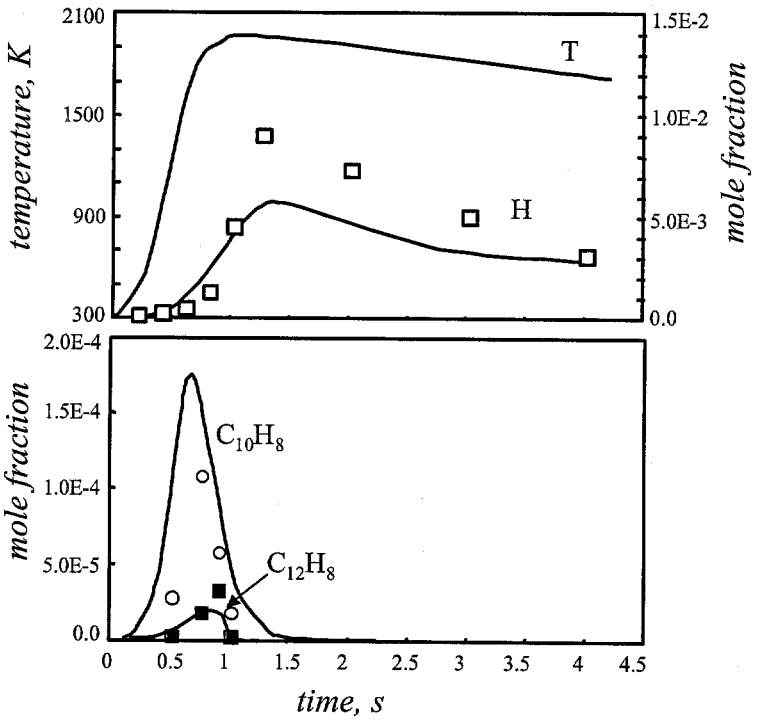


Fig. 1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900
300
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0.0
mole fraction
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H
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1.5E-4
1.0E-4
5.0E-5
0.0
mole fraction
$C_{10}H_8$
$C_{12}H_8$
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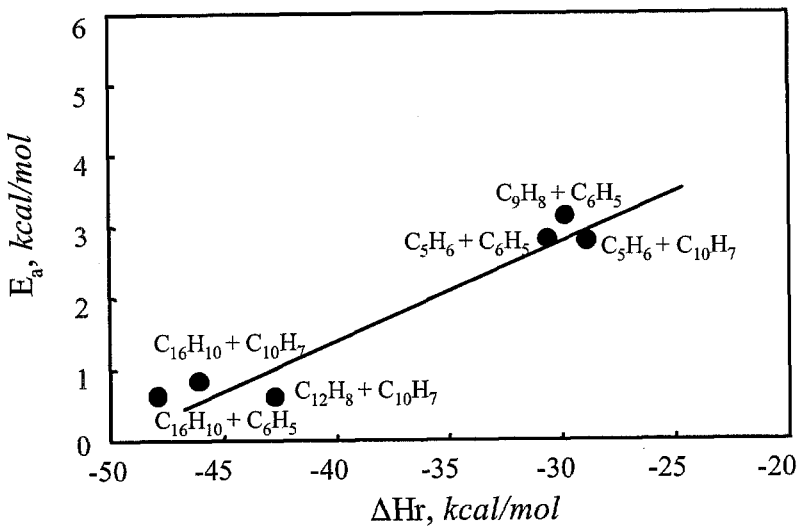
4
4.5
time, s

Fig. 2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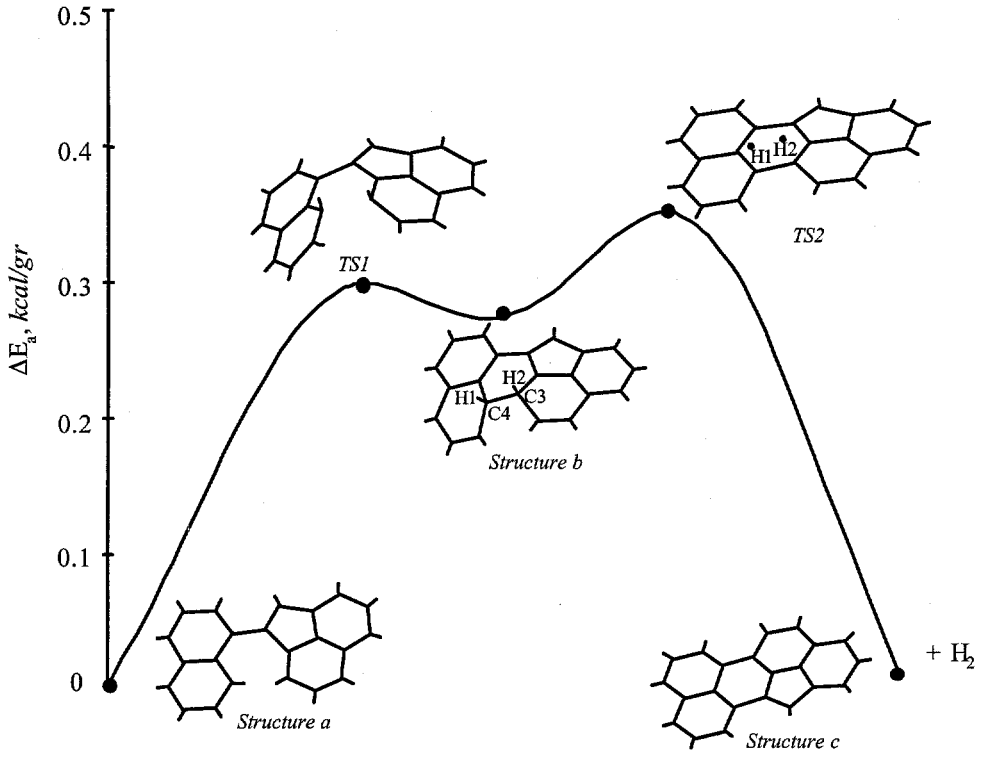
$C_5H_6 + C_{10}H_7$
$C_{16}H_{10} + C_{10}H_7$
$C_{12}H_8 + C_{10}H_7$
$C_{16}H_{10} + C_6H_5$

Fig. 3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Structure c
+ H_2

Fig. 4

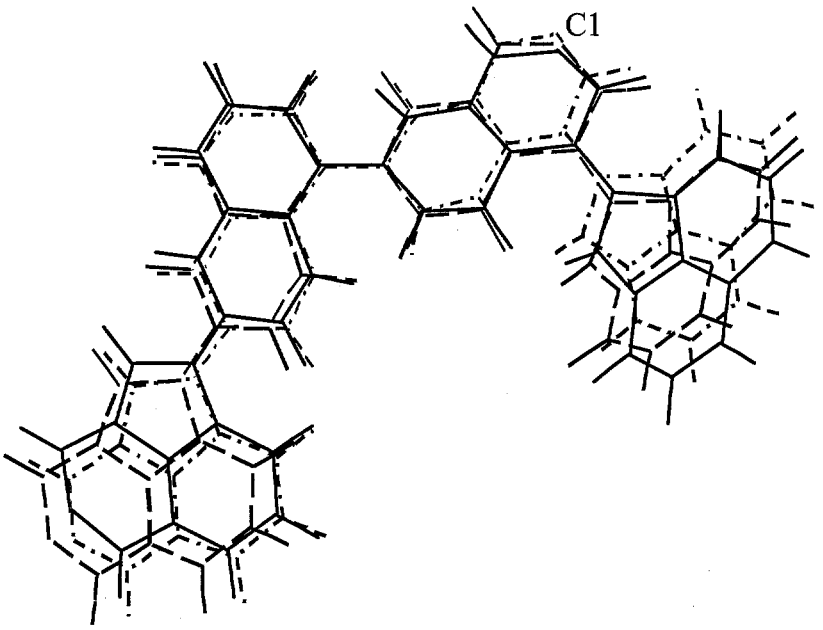

Fig. 5

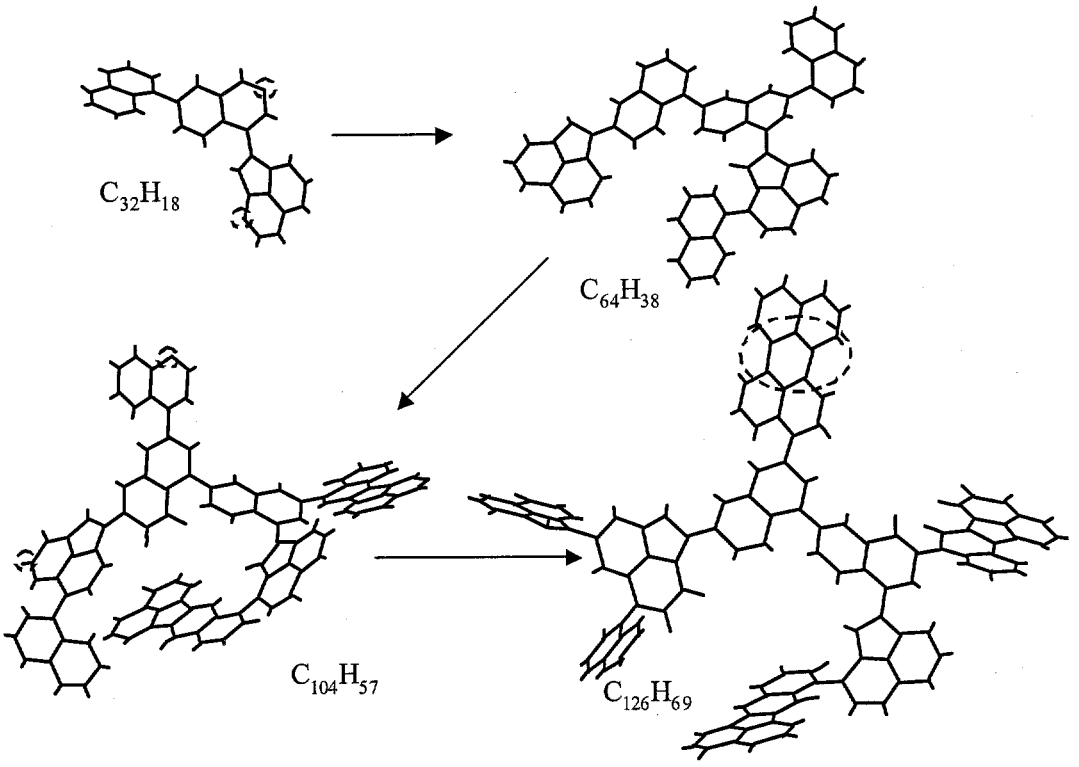

Fig 6